

**DEUS** **B05** 83-736079/33 = J8 6013-704-B  
3-carboxy:methyl-cysteine optical resolution - by selective crystallisation of the s- and r enantiomers from a supersaturated soln. of the ammonium salts of the mixed enantiomers  
DEGUSSA AG 26.03.82-DE-211127  
DZI E16 (15.04.86) \*DE321127-C C07b-57 C07c-148/04 C07c-149/24

24.03.83 as 048051 (280SC)  
In the prodn. of S-(carboxymethyl) -(R)-cysteine (R-(I)) and S-(Carboxymethyl)-(S)-cysteine (S-(I)) from a mixt. of the two enantiomers, (A) the mixt. is dissolved in water in the presence of ammonia in an amt. such that the resulting soln. of the ammonium salts has a pH of 6-9; (B) the soln. is rendered supersatd. (C) one of the two enantiomers ammonium salts is crystallised by addn. of seed crystals of the ammonium salt of one of the enantiomers (provided that when the starting mixt. contd. an excess of one of the enantiomers, then the seed crystals added were of the ammonium salt of that enantiomer); (D) the pptd. crystals are sepd. off; (E) the ammonium salt of the other enantiomer is crystallised by adding seed crystals of this enantiomers ammonium salt to the mother liquor; (F) the pptd. crystals are again sepd., and (G) S-(I) or R-(I) is fixed from the corresp. ammonium salt.

Prods., esp. the (R)-enantiomer, are useful as pharmaceutical active substances, as well as in the cosmetics industry (e.g. in the prodn. of hair fixatives). (J58172365-A) (6pp)

**RIKA** **B05** 83-791052/43 = J8 6013-634-B  
Alpha, beta-unsatd. ketone(s) mfr. - from carbon monoxide, hydrogen acetylene cpd. and olefin in presence of rhodium metal or pharmaceutical agrochemical  
RIKAGAKU KENKYUSHO 02.03.82-JP-032537  
COS E19 (15.04.86) \*J58150533-A C07c-45/49 C07c-49/20 C07c-69/73 + B01j-23/46 B01j-31/16

02.03.82 as 032537 (57WB)  
Method comprises reacting CO, molecular, hydrogen, acetylene cpd. of formula R1-CC-R2 (where R1 and R2 are each H, alkyl, aryl, allyl, alkoxy carbonyl, acyl, alkoxyalkyl, or hydroxyalkyl gp.), and olefin cpd. of formula CH2=CH-R3 (where R3 is H, alkyl, alkoxy carbonyl, aryl, acyloxy, alkoxy gp., acyl gp., cyano gp., or halogen), in the presence of Rh metal or Rh cpd. catalyst to obtain alpha, beta-unsatd. ketone of formula R4CH=CR5-COR6 (where R4=R1 and R5=R2 or R4=R2 and R5=R1; R6 is -CH2CH2R3 or -CH2R3-CH3. The acetylene cpd. is e.g. acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, etc. The olefin cpd. is e.g. ethylene, propylene, 1-butene, etc. The Rh cpd. is, e.g., Rh4(CO)12, Rh6(CO)16, Rh2(CO)4Cl2, etc.

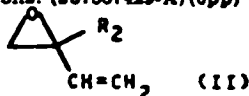
Alpha, beta-unsatd. ketones are obtd. selectively and are useful as raw matls. for pharmaceuticals, agrochemicals, etc. (J58150533-A) (6pp)

**SUMO** **B05** 81-42377D/24 = J8 6013-690-B  
Stereospecific prodn. of Z-isomers of allylic alcohol derivs. - from vinyl epoxide and organo-lithium cpd., useful intermediates for pharmaceuticals, agrochemicals, perfumes etc.  
SUMITOMO CHEM IND KK 13.06.80-JP-080413  
COS E19 (15.04.86) \*EP-29603-A B01j-31/02 C07c-29/36 C07c-33/03

13.06.80 as 080413 (CC)  
Prodn. of predominantly Z-allylic alcohols of formula R1CH2CH:CH(R2)CH2OH (I) comprises reacting epoxides (II) with an organolithium cpd. R1-Li (III) (where R1 is opt. subst., (un)branched 1-25C alkyl which can have one or more unsatd. bonds, pref. alkyl, alkenyl, aralkyl or 10C polycyclic hydrocarbyl; R2 is H or methyl).

Cpds. with R2 as methyl and R1 as sec-butyl, iso-butyl, cyclopropyl, cyclohexyl, 2-phenethyl or 2,2-ethylenedioxy-1,7-dimethy-bicyclodimethyl bicyclo(2,2,1)heptyl-7-methyl are new.

USE/ADVANTAGE - (I) are useful as intermediates for pharmaceuticals, agricultural chemicals, perfumes etc. The Z-form of (I) is produced selectively in good yield in a single stage under mild reaction conditions. (J57007429-A) (6pp)



**BLAS** **B05** 83-15329K/07 = J8 6013-634-B  
Aryl-alkanolic acids prepa. by rearrangement of alpha-halo ketone(s) - in protic medium using non-noble metal salt catalyst  
BLASCHIM SPA 23.07.81-IT-023085  
(15.04.86) \*EP-71299-A B01j-27/13 C07b-41/08 C07c-57/32 C07c-59/64 C07c-69/81 C07d-333/24

21.07.82 as 127434 (949RP)  
Prepn. of alkanolic acids RR'RC-OOY (I) comprises rearrangement of alpha-halo ketones RCOCXR'R (II) in protic medium in the presence of a non-noble metal salt, hydrolysing the prod. if it is an ester to give the corresp. acid: (where R is opt. subst. aryl, opt. subst. heterocyclic or a fused arylheterocyclic system; R' and R are each H, 1-10C alkyl, benzyl or a value of R; X is halogen; and Y is H or 1-6C alkyl). Pref. protic medium is water or a 1-6C aliphatic alcohol. Pref. metal salts are of non-noble transition metals, esp. a Zn halide. Reaction may be in presence of a diluent.

(I) are useful as intermediates or as e.g. antiinflammatory, analgesic and antipyretic agents, esp. ibuprofen, fenclozac, indoprofen, naproxen, ketoprofen, tolmetin, etc. Other (I), e.g. thienyl acetic acid, may be used as intermediates to semi-synthetic penicillins or cephalosporins or other antiinflammatories, e.g. thlaprofen acid. The process avoids the use of expensive noble metal catalysts (see e.g. GB 2042543, J58024526-A) (4pp)

**BANY** **B02** 78-11067A/06 = J8 6013-479-B  
Crystallisation of cefalexin hydrate - by contacting cefalexin with heated aq. soln. contg. (in)organic acid salt  
BANYU PHARM CO LTD 14.06.78-JP-068768  
(14.04.86) \*J52153991-A C07d-501/22

14.06.78 as 068768 (38MD)  
Process for crystallising prismatic crystals of cefalexin hydrate comprises contacting cefalexin with aq. soln. contg. salt of (in)organic acid (e.g. salt of HF, HCl, HBr, HNO3, HCOOH or AcOH, or a mixture esp. HCl) to form prismatic crystals of cefalexin hydrate. Temp. of the aq. soln. is 58 deg.C to temp.-necessary to allow crystallisation out of prismatic crystals of cefalexin hydrate from the aq. soln. (e.g. 57 deg.C at 8,000 ppm Cl(-); 30 deg.C at 42,000 ppm or 15 deg.C at 121,000 ppm). Aq. soln. is esp. 2-10% and 2-10 times w.t. wt. of cefalexin.

Process provides stable cefalexin crystals with little hygroscopicity and no static charge. (J52153991-A) (5pp)

**ELIL** **B02** 77-82879Y/35 = J8 6013-477-B  
Cephalosporins prepa. from e.g. (3)-cephem sulphoxides - by using acyl bromide and bromine scavenger  
ELILILLY & CO 09.06.78-US-694516  
(14.04.86) \*US4044002-A C07d-501/04

08.06.77 as 068373 (1248WD)  
Cephalosporin sulphoxides (I) are reduced to the corresp. cephalosporins (II) by treatment in an inert solvent at -25 deg.C to 50 deg.C with at least 2 molar equivs. per mole (I) of an acyl bromide R3COBr (where R3 is 1-10C alkyl opt. subst. by halogen, CN, Ph, 1-4C alkoxy or 2-5C alkoxy carbonyl, Ph opt. subst. by halogen, CN, NO2, 1-4C alkyl, 1-4C alkoxy or 2-5C alkoxy carbonyl; or 3-8C cycloalkyl) in presence of a Br scavenger. (I) is a 3-cephem or 3-exomethylene cepham cpd.

(II) are useful antibacterials and intermediates and they are obtd. by the efficient redn. of (I).

In an example, p-nitrobenzyl 7-phenoxyacetamido-3-methyl-3-cephem-4-carboxylate sulphoxide in CH2Cl2 contg. 2-methyl-2-butene was treated with acetyl bromide to reduce the sulphoxide. (J52151193-A) (17pp)

**HOFF** **B05** 76-97408X/32 = J8 6013-454-B  
Carotenoid inters. prepa. from 3-alkoxy cycloalk 2-enones - by Grignard reaction with alkenyne deriva.  
HOFFMANN-LA ROCHE AG 09.06.73-US-585224  
D13 E24 (14.04.86) \*NL7606160-A C07c-45/67 C07c-49/64 C07c-173 C07i-09/34

08.06.76 as 066163 (CC)  
Prepn. of cyclic oxo cpds. is carried out by (a) reacting a cyclic ketone of formula (I) (where R is 3-8C alkyl; n = 0 or 1) with a Grignard reagent of formulae (IIa) or (IIb) (where Y is alkali metal or MgX; X is halogen; R1 is OH or a hydrolysable ether gp.) to form a prod. of formula (IIIa) or (IIIb); and (b) opt. converting the prod. into a carotenoid cpd. of formula (IV); viz. canthaxanthene (n = 1) and dinorcanthaxanthene (n = 0) are useful as food dyes. (J51149249-A) (18pp)

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